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USE OF A POLYACETYLENE CATHODE IN PRIMARY
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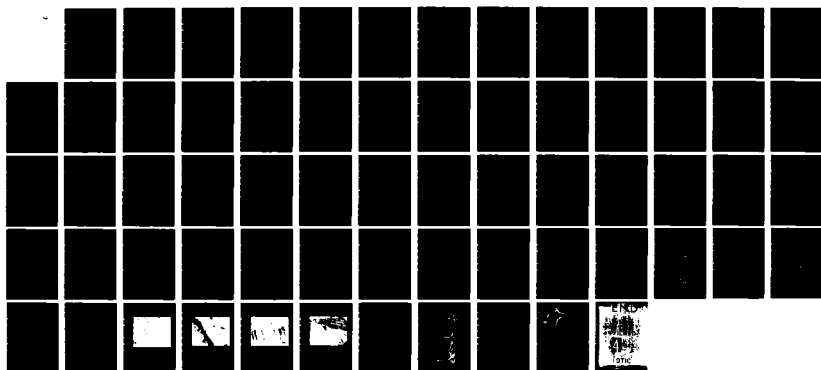
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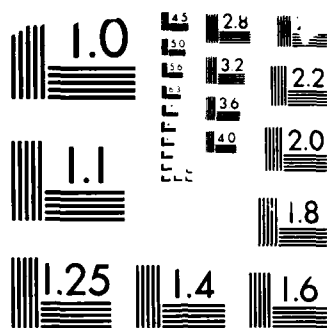
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GC-TR-83-281

USE OF A POLYACETYLENE CATHODE
IN PRIMARY LITHIUM-THIONYL
CHLORIDE CELLS

PREPARED FOR
U.S. NAVAL RESEARCH LABORATORY
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GEO-CENTERS, INC.

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GENERAL INTRODUCTION

This report describes the work performed by Geo-Centers for the Navy with regard to the use of poly(acetylene), $(CH)_x$, as a cathode material in a lithium/thionyl chloride ($Li/SOCl_2$) battery. The objective of the project was three-fold:

- (1) To characterize and understand the electrochemistry of $(CH)_x$ in a detailed manner.
- (2) To study the compatibility of $(CH)_x$ with $SOCl_2$.
- (3) To synthesize and investigate "modified" $(CH)_x$ polymers which may possess more desirable properties than the parent polymer.

Part I of the report is concerned with the exposure of $(CH)_x$ to $SOCl_2$. The discovery that $SOCl_2$ can dope $(CH)_x$ to the metallic state is noted; the chemical and physical properties of the doped polymer are described.

Part II deals with the properties of several complexes of ruthenium which are capable of undergoing electrochemical polymerization to form thin films. Two of the complexes are new and contain polymerizable acetylenic functional groups. Despite the theoretical structural similarity of the metallopolymer film backbone to poly(acetylene), the thin complex films are found to

be poor conductors. The electrochemical and other physical characteristics of the metal complex monomers and polymers is explored in detail.

The electrochemical behavior of $(CH)_x$ films in non-aqueous media was also investigated by cyclic voltammetry, coulometry and potential step chronoamperometry. The salient results have been incorporated into Parts I and II of this report. A more comprehensive description of the results will be presented in a subsequent report.

PART I. THIONYL CHLORIDE DOPING OF POLY(ACETYLENE)

1. INTRODUCTION

The conversion of neutral, semiconducting poly(acetylene), or $(CH)_x$, to the metallic state has been accomplished in a variety of ways (1). Chemical, electrochemical and photochemical techniques have been employed to effect the redox processes which produce the conductive n- and p-doped materials. In this report, the doping of $(CH)_x$ by exposure to thionyl chloride is described. The choice of $SOCl_2$ as a dopant was based partly upon the fact that $SOCl_2$ is a volatile, oxidizing solvent which could readily penetrate the $(CH)_x$ fibrils, dope the polymer uniformly and then be easily removed under vacuum.

Silvery poly(acetylene) film, prepared using a modified Shirakawa procedure (2), was transferred (as ca. 2.5 mm x 0.5 mm strips) under He to an equilibration flask which was then attached to a high vacuum line. Previously freeze-pump-thaw degassed $SOCl_2$ was trap-to-trap distilled as a colorless liquid into the $(CH)_x$ -containing flask until the polymer was completely covered by liquid. After 3 hours' exposure, the slightly yellow $SOCl_2$ was pumped away from the now homogeneously golden $(CH)_x$ and the film was left under dynamic vacuum for 18 hours. The thickness (measured by micrometer) of the still-flexible films was found to have increased from 76 to 99 microns upon doping.

The first piece of evidence that $SOCl_2$ had successfully doped the $(CH)_x$ came from the color change of the film. The golden

luster is characteristic of metallic $(CH)_x$. An infrared spectrum of the untreated film matched the IR reported in the literature (2). The relative intensities of the C-H out-of-plane deformation modes for the cis- (740 cm^{-1}) and trans- (1015 cm^{-1}) components of the polymer allowed calculation of the cis/trans ratio for the room temperature, thermally equilibrated sample used in this work as 53% cis/47% trans. However, the spectrum of the doped polymer exhibited 0% transmission throughout the infrared region, a result typically associated with free carrier absorption or reflection of the incident light by a metallic sample (3).

Film conductivities were determined using the four-point probe method (4). Values for the doped materials were $1.7 - 1.8 \times 10^{-3}\ \Omega^{-1}\text{ cm}^{-1}$, five orders of magnitude greater than that obtained for the untreated $(CH)_x$ ($\sigma = 2 \times 10^{-8}\ \Omega^{-1}\text{ cm}^{-1}$). Compared to the conductivities of up to $\sim 10^3\ \Omega^{-1}\text{ cm}^{-1}$ which have been obtained using other p-type dopants (1a), the value obtained here is relatively low. However, it may be possible to improve the conductivity of the $SOCl_2$ -doped polymer by the use of higher quality starting material (see Elemental Analysis Section below) and optimization of the doping procedure, in particular, the time for exposure of the $(CH)_x$ to $SOCl_2$.

Scanning electron microscopy of the doped materials revealed no apparent damage to the internal fibrillar structure of the film as a consequence of the doping reaction.

The formation of metallic $(CH)_x$ upon exposure to $SOCl_2$ was also investigated by EPR spectroscopy. As the doping reaction progressed, the initially narrow $(CH)_x$ signal at $g = 2.0096$ and linewidth (ΔH) = 1.6 Gauss gradually evolved into a broader signal at $g = 2.0091$, $\Delta H = 3.1$ Gauss. This effect has been observed previously in samples of metallic $(CH)_x$ and was attributed to the susceptibility of the Π -electrons in the conducting system (5). A

pseudo first-order plot of signal intensity vs. time gave a value of $k \approx 10^{-5}$ to 10^{-6} sec^{-1} for the rate constant of the doping reaction.

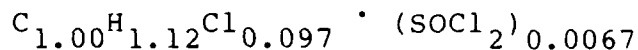
Elemental analyses (Galbraith Laboratories, Knoxville, Tennessee) were performed on the polymers and analytical results were as follows:

Undoped sample: Calc: C, 93.3; H, 6.7

Found: C, 86.38; H, 7.89. Total = 94.27%

Doped sample: Found: C, 66.45; H, 6.27; S, 1.19; Cl, 21.46.

Assuming that the origin of S is residual trapped SOCl_2 , the empirical formula of the doped polymer can be written as:



The inclusion of O (from SOCl_2) brings the total accountable percentage of elements to 95.96%. The discrepancy in the C/H ratio of the doped polymer is disturbing, but the C/H ratios of the doped and undoped samples are within 3%, indicating that the source of the discrepancy lies in the starting material and is not caused by the doping process.

The empirical formula calculated for the doped polymer shows incorporation of 9.7% Cl relative to C. With the knowledge that SOCl_2 is an oxidizing solvent and that its electrochemical reduction results in liberation of Cl^- (6), it is proposed that exposure of $(\text{CH})_x$ to SOCl_2 has resulted in partial chemical oxidation of the polymer to poly(carbonium) sites, with charge compensation provided by the Cl^- formed upon SOCl_2 reduction.

To complement the elemental analysis data, the doped films were characterized by x-ray photoelectron spectroscopy (XPS). The

elemental composition of the sample was found to include C, O and Cl (H is not detectable by XPS). No evidence for S was observed. The carbon 1s peak was symmetric and reflected only a single chemical environment for the carbon atoms. In contrast, poly-(vinylchloride) (PVC), which has covalently bound Cl on alternating carbons displays a split, two-component C 1s peak in the XPS spectrum (7). Chlorine is present in the sample, as evidenced by the presence of the Cl 2s and 2p peaks. On a semi-quantitative basis, the XPS indicates Cl doping of the $(CH)_x$ to a level of $(15 \pm 5)\%$. There was not sufficient data to determine unambiguously the oxidation state of chlorine. The Cl 2s peak was complex, with considerable structure, whereas the Cl 2p was a single, narrow peak. The corresponding Cl 2p peak in PVC is known to be a doublet. Also, the carbon 1s-chlorine 2p energy difference is ~ 1 eV greater in the doped $(CH)_x$ than in PVC, indicating that the chlorine is more likely present as $(Cl_n)^-$ ($n = 1$ or 3) in the doped polymer than as covalent Cl. However, more detailed studies with appropriate reference materials are needed.

The lack of any peaks due to sulfur in the sample is not surprising. The formulation of the doped polymer is proposed to contain 0.67% of S as $SOCl_2$, presumably as trapped solvent. It is entirely possible that the ultra-high vacuum used in the XPS experiment removed the remaining $SOCl_2$. Also, XPS is a surface-sensitive technique which probes only the outer ~ 50 Å of the film -- the region most likely to be depleted of any trapped volatiles.

The relatively large amount of oxygen in the sample -- approximately 10 to 15%, calculated from the ratio of the oxygen 1s to carbon 1s peaks -- is not encouraging. The O 1s peak is a narrow singlet, indicating only one type of oxygen atom environment. It cannot be determined at this time whether the origin of the oxygen is trapped H_2O , or, more likely, oxidized carbon functionalities in the parent and/or doped polymer such as >C-OH or >C=O .

The doped films were examined by cyclic voltammetry in an He atmosphere glove box using 0.1 M tetra-n-butylammonium perchlorate/propylene carbonate electrolyte. The open-circuit potential ($V_{oc} = -0.28$ V) was used as the initial potential. The potential was then swept between V_{oc} and +2.0 V. The i - E response was a straight line through the origin, characteristic of the film acting as a resistor. There was no evidence for the Cl^-/Cl_2 couple, which would be expected from oxidation of electrostatically-bound chloride ion. The film resistance was calculated from the CV to be about 50 k Ω , yielding film conductivities in the range 10^{-3} to 10^{-2} Ω^{-1} cm $^{-1}$ - values similar to those obtained by the four-point method described above. The voltammetry of pristine $(CH)_x$ films of the same thickness as that used in the doping experiments was also featureless. In contrast, the CV of thin films of undoped $(CH)_x$ when examined under similar conditions shows distinct features, corresponding to the $(CH)_x^{+0}$ couple at $E^{0'} \approx +0.8$ V vs. Pt (8). Subsequently, the negative limit of the potential sweep was extended to -2.0 V. Again, only the straight line was obtained. No process corresponding to $(CH)_x^+ \rightarrow (CH)_x$ (undoping) was observed. In an attempt to examine the electrochemical response of an external redox couple at the doped polymer electrode, $[Ru(bpy)_3]^{2+}$ ($bpy = 2,2'$ -bipyridine) was added to the electrolyte solution. However, none of the four easily accessible couples of the complex $E_{1/2} = +1.17, -1.41, -1.58, -1.81$ V vs. Pt) were detected. The explanation for the inability to observe the electrochemical processes in the thick films described above must be due to uncompensated IR losses in the film.

In summary, $SOCl_2$ has been found to be effective as a p-type dopant for the preparation of metallic poly(acetylene). The use of this material, as well as other oxyhalide-doped $(CH)_x$ products, in electrochemical applications is currently being investigated.

Table 1. Properties of $(CH)_x$ Before and After Exposure to $SOCl_2$.

	Undoped	Doped
Film Color	Silver	Gold
Conductivity	$2 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$	$1.2 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$
IR	60% cis/40% trans	Blank - metallic spectrum
Elemental Analysis	$C_{1.00}H_{1.09}$	$C_{1.00}H_{1.12}Cl_{0.097} \cdot (SOCl_2)_{0.0067}$
Cyclic Voltammetry	$E^{O'} = 0.8 \text{ V}$	IR drop only
EPR	$g = 2.0096$ $\Delta H = 1.6 \text{ Gauss}$	$g = 2.0091, \Delta H = 3.1 \text{ Gauss}$
XPS		Detected C, O, Cl; no S Cl as Cl^- or Cl_3^-

PART II. SPECTRAL, ELECTROCHEMICAL AND CONDUCTIVITY
STUDIES OF POLY(PYRIDYL) RUTHENIUM COMPLEXES
CONTAINING POLYMERIZABLE ACETYLENIC AND
OLEFINIC LIGANDS

1. INTRODUCTION

Modification of electrode surfaces with insoluble, electro-active polymer coatings is currently an area of considerable interest due to the diversity of applications potentially afforded by such tailor-made interfaces (9-11). Reductive electrochemical polymerization (EP) of transition metal complexes containing bound ligands with polymerizable functional groups (9,11) has been found to be a relatively simple technique for producing stable, electro-active and reasonably uniform films as homopolymers, copolymers or spatially segregated bilayers. A recent study (9) extended to over 30 the number of polymerizable complexes and examined the mechanisms involved in the EP process. A common feature of the metallopolymer films prepared to date by this method is that they are derived from monomer complexes which possess an olefinic site on at least one of the ligands of the molecule. An example is the prototype monomer $\text{cis}[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$, (bpy = 2,2'-bipyridine, vpy = 4-vinylpyridine).

In contrast to other electrochemically polymerized films which passivate the electrode (12) or are electronic conductors (e.g., poly(pyrrole)) (13), films formed from the bis(vpy) complex and similar molecules are redox conductors (11a,b,m). Reductive coupling of the vinylic monomers gives rise to polymers composed of non-interacting metal sites linked by a saturated hydrocarbon backbone. The conductivity of these films depends on redox reactions within them and involves both electronic motion within a narrow band at energy levels corresponding to the polymeric metal

complex redox potentials and ionic motion to preserve charge neutrality within the film. Some doped polymers such as poly(pyrrole) and poly(acetylene) (14), or $(CH)_x$, conduct electronically quite well, with σ up to $3000 \Omega^{-1}cm^{-1}$ (14b). In an attempt to create a metallopolymer film with a conjugated backbone and possibly endow the film with the additional feature of electronic conductivity, the acetylenic-ligand containing metal complex monomers $cis-[Ru(bpy)_2(py_2C_2)_2]^{2+}$, (py_2C_2 = bis(4-pyridyl)acetylene) and $mer-[Ru(trpy)(py_2C_2)_3]^{2+}$, (trpy = 2,2',2"-terpyridine) have been synthesized. With the knowledge that related organic monomers such as diphenylacetylene can be reductively polymerized in non-aqueous media (15), the electrochemistry of the bis(pyridyl)acetylene complexes and their polymer analogues was investigated. Two-point conductivity measurements on the polymer coated electrodes are reported.

The spectral and redox properties of the py_2C_2 complexes are also compared to complexes with similar polymerizable ligands in two homologous series: $[Ru(bpy)_2(L)_2]^{2+}$ and $[Ru(trpy)(L)_3]^{2+}$, where $L = vpy$, py_2C_2 and BPE (BPE = trans-1,2-bis(4-pyridyl)-ethylene, see Figure 1).

2. EXPERIMENTAL PROCEDURE

(a) Materials

Acetonitrile (Burdick & Jackson) for electrochemical measurements was stored over activated Davison 3A molecular sieves for at least 24 hours before use. Tetra-n-ethylammonium perchlorate (TEAP) and tetra-n-butylammonium hexafluorophosphate (TBAH) were obtained from Southwestern Analytical Chemicals, dried in a vacuum oven for 12 hours at 60°C and stored in a desiccator. Bis(4-pyridyl)acetylene (King's Mountain Specialties, King's Mountain, North Carolina) was found to match the literature melting point as well as infrared and NMR spectra (16). $[\text{Ru}(\text{bpy})_2(\text{vpy})_2](\text{PF}_6)_2$, $[\text{Ru}(\text{trpy})(\text{vpy})_3](\text{PF}_6)_2$ and $[\text{Ru}(\text{trpy})(\text{BPE})_3](\text{PF}_6)_2$ were prepared as described in the literature (9). All other chemicals and solvents were reagent grade or better and were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

(b) Preparation of cis- $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2](\text{PF}_6)_2$

Cis- $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (100 mg, 0.19 mmol) (17) was added to 20 ml of an N_2 -degassed 1:1 (v/v) ethanol/water solution of bis(4-pyridyl)acetylene (210 mg, 1.17 mmol). The mixture was protected from light (18) and heated under N_2 at gentle reflux for 5 hours. After cooling to room temperature, 0.5 ml of saturated aqueous NH_4PF_6 solution was added and the resulting orange precipitate was filtered, rinsed with water, diethyl ether and then dried. The solid was purified by column chromatography on basic alumina (Fisher). A minor red-brown band, probably $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)\text{Cl}]^+$,

was eluted with 1:1 acetonitrile/toluene before the major orange fraction ($\lambda_{\text{max}} = 393 \text{ nm}$) was collected using a 2:1 CH_3CN /toluene mixture. A second orange (likely thermal polymerization (19)) component remained near the top of the column. Solvent was removed by rotary evaporation and the product isolated by reprecipitation from CH_3CN into stirring ether. Yield: 70 mg (35%). Elemental analysis calculated for $\text{RuC}_{44}\text{H}_{32}\text{N}_8\text{P}_2\text{F}_{12} \cdot 2\text{H}_2\text{O}$: C, 48.02; H, 3.30; N, 10.19. Found: C, 47.87; H, 3.40; N, 10.18. (Note: the inclusion of one water of hydration per py_2C_2 ligand in the bis- and tris- py_2C_2 complexes has been observed for the structurally similar BPE complexes (20).)

(c) Preparation of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{BPE})_2](\text{PF}_6)_2$

This complex was prepared using the same procedure as described above for the pyridylacetylene complex, with the substitution of the BPE ligand for py_2C_2 . The properties of the complex produced by this method were identical to those observed previously (9) when a different synthetic route was employed (20). Yield: 58%.

(d) Preparation of $\text{mer-}[\text{Ru}(\text{trpy})(\text{py}_2\text{C}_2)_3](\text{PF}_6)_2$

This complex was prepared similarly to other $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ complexes reported in the literature (9). Purification by column chromatography gave the desired product as an orange-brown solid in 35% yield. A minor red-brown component, likely $[\text{Ru}(\text{trpy})(\text{py}_2\text{C}_2)_2\text{Cl}]^+$, eluted prior to the main band and was isolated in 10% yield. Elemental analysis calculated for $\text{RuC}_{51}\text{H}_{35}\text{N}_9\text{P}_2\text{F}_{12} \cdot 3\text{H}_2\text{O}$: C, 50.2; H, 3.39; N, 10.35. Found: C, 48.4; H, 3.38; N, 10.45.

(e) Electrodes, Instrumentation and Electrochemical Procedures

Before each experiment, Kel-F shrouded platinum disk electrodes (Bioanalytical Systems, West Lafayette, Indiana, 0.0177 cm^2 area) were mechanically polished with diamond paste (Buehler) to a 1/4 micron finish then cleaned electrochemically (21) by anodizing

and cycling in 1 M H_2SO_4 . Electrochemical instrumentation included a PAR Model 174A Polarographic Analyzer and a PAR Model 175 Universal Programmer. Electrochemical experiments were performed in a fritted, three-compartment cell of conventional design. Measurements are referenced to a sodium chloride saturated calomel electrode (SSCE). A platinum wire served as the auxiliary electrode.

Electrolyte solutions were 0.1 M TEAP/ CH_3CN with the concentration of complex added being ca. 1 mM for the $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ series and ca. 2 mM for the $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ complexes. In the case of $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^{2+}$, the electrolyte solution for the film formation experiments was 0.1 M TBAH/ CH_3CN due to the low ($<10^{-3}$ M) solubility of the complex in perchlorate electrolyte. Solutions of the bis(L) complexes were protected from light to avoid photosubstitution (18). Film formation was accomplished by cycling the working electrode potential at 200 mV/s repeatedly from 0 V to ca. 150 mV past $E^{o'}$ for the oxidative or reductive couple of interest. When the reverse component of the wave was not well-defined, the potential limit was set at about 100 mV past the peak potential, E_p . After film formation, the electrode was rinsed with acetone, air-dried and its electrochemical response examined in fresh TEAP/ CH_3CN electrolyte. The coverage of electroactive material, Γ , was determined from the charge under the anodic M(III/II) wave under linear peak current vs. sweep rate conditions.

The intrinsic polymerizability of a complex, Γ/Γ_o , was calculated by normalizing the measured coverage for the concentration of monomer complex in solution and the number of cycles used to produce the film, then dividing by the coverage obtained ($6.6 \times 10^{-9} \text{ mol/cm}^2$) for the arbitrarily chosen standard complex, $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$. This procedure was used for films formed by either oxidative or reductive cycling. The polymerization

efficiency, Φ_{poly} , was calculated from the measured coverage of electropolymerized complex divided by the amount of monomer complex undergoing redox per cycle, times the number of cycles employed (22). Although the electrochemical properties of the vpy and BPE complexes have been described in an earlier report (9), experiments were repeated using independently synthesized materials. The results given here are summarized from the cumulative data of both the previous and present investigations.

IR compensation was used in chronoamperometry experiments to eliminate distortions in the i - t response due to the effects of uncompensated film resistance. I - t transients were recorded on a Hewlett-Packard storage oscilloscope.

Scanning electron micrographs of a poly- $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$ coated Pt foil were obtained by cementing the foil with conductive silver paint (SPI Supplies, West Chester, Pennsylvania) to an aluminum specimen mount, which was then examined in an AMR 1000 microscope.

Two-point conductivity measurements were made on dry poly- $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$ coated disk electrodes using a Keithley Model 616 Digital Electrometer. Contact to the open film surface was made by immersing the electrode in a mercury pool. A copper wire completed the circuit. The films in Hg spontaneously generated an open circuit voltage, V_{oc} , of 0.3 - 0.7 V. Two approaches were employed to determine film resistance, R_f : (1) after measuring V_{oc} , the load resistance, R_l , through the electrometer was progressively lowered until the measured voltage was 0.5 V_{oc} . At this point, $R_l = R_f$. (2) The electrometer was used to pass progressively increasing currents through the film. At sufficiently large I , $V \gg V_{\text{oc}}$ and R_f can be calculated from $(V - V_{\text{oc}})/I$. Attempted four-point measurements on a Pt foil coated with the same polymer were unsuccessful, probably due to puncturing of the film by the probe head and/or high film resistance.

Conductivity measurements on a mixed valence poly-[Ru(bpy)₂-(py₂C₂)₂]^{2+/+} film were performed in a He-filled dry box (Vacuum Atmospheres Company) using the following procedure. The coated Pt disk was immersed in TEAP/CH₃CN electrolyte and the applied potential was set to E^{o'} for the first complex reduction, thereby producing a film with equal numbers of 2+ and + Ru complex sites. When the current for the reduction reaction decayed to zero, the potentiostat was switched to open circuit, the coated electrode was removed from the electrolyte, rinsed briefly with CH₃CN and shaken dry. Conductivities were then obtained using methods 1 and 2 described above.

UV-Vis spectra were recorded on a Cary 14 spectrophotometer. Spectra and electrochemical data were digitized and plotted using an H-P 9872B Plotter.

3. RESULTS AND DISCUSSION

(a) The Disubstituted Complexes, $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ (L = vpy, BPE, py_2C_2): Spectral Properties

Figure 2 shows the UV-Vis spectra of the bis(L) complexes in acetonitrile solution which exhibit a manifold of transitions between 500 and 350 nm. λ_{max} values are listed in Table 2. In accordance with the spectral assignments of many other poly(pyridyl)ruthenium(II) complexes in the literature (17,23), these bands are assigned as MLCT $\Pi^*(\text{bpy}) \leftarrow \text{Ru}(\text{d}\Pi)$ and $\Pi^*(\text{L}) \leftarrow \text{Ru}(\text{d}\Pi)$ transitions. The most significant difference among the spectra is the blue shift of the highest energy transition of the bis-vpy complex ($\lambda_{\text{max}} = 358$ nm) relative to the maxima of the BPE and py_2C_2 complexes, which occur at about 400 nm. This would be consistent with the assignment of these bands as the metal-to-polymerizable ligand transition since greater delocalization of the excited electron in the BPE and py_2C_2 ligands would be expected to lower the transition energy. Also, the presence of the electron-withdrawing pyridyl "substituent" on the bound pyridyl group of the BPE and py_2C_2 ligands may contribute towards lowering the energy of the $\Pi^*(\text{L})$ orbital. There is a smaller difference between the $\text{Ru} \rightarrow \text{L}$ transitions in the BPE (405 nm) and py_2C_2 (398 nm) complexes which may be attributable to the greater Π -donating ability of the acetylenic, as opposed to olefinic, substituent. Thus, the UV-Vis spectra show that the relative ordering of the three ligands in terms of their overall Π -accepting ability is $\text{BPE} > \text{py}_2\text{C}_2 \gg \text{vpy}$. The reduction potentials

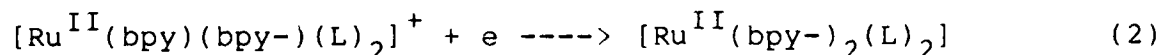
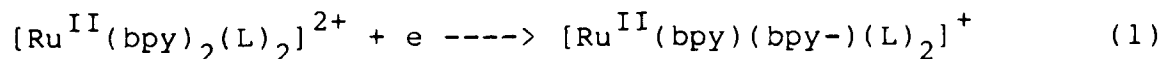
Table 2. Spectral Properties of the Complexes in CH₃CN Solution.

	λ_{max} (nm)
$[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$	465, 434, 358
$[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^{2+}$	460(sh), 427, 395(sh)
$[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$	455(sh), 425, 393(sh), 375(sh)
$[\text{Ru}(\text{trpy})(\text{vpy})_3]^{2+}$	501, 372
$[\text{Ru}(\text{trpy})(\text{BPE})_3]^{2+}$	501, 405
$[\text{Ru}(\text{trpy})(\text{py}_2\text{C}_2)_3]^{2+}$	490(sh), 398

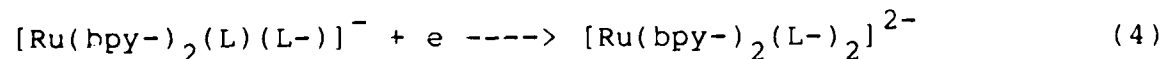
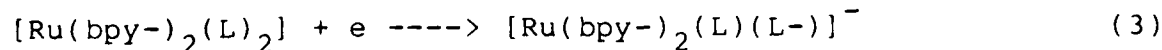
of the free ligands (shown in Table 3), measured as $E_{p,c}$ for the irreversible L(0/-) processes, corroborate the ordering determined from the spectra.

(b) Electrochemistry

Cyclic voltammograms (CVs) of the $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ complexes in acetonitrile solution are shown in Figure 3; formal potentials for the oxidative and reductive couples are summarized in Table 4. The Ru(III/II) couples $E^{\circ'}(\text{ox}, \text{soln})$, are reversible ($\Delta E_p = 60 - 70$ mV) and occur between +1.24 and +1.32 V. Potentials for the first and second reductions (designated $E^{\circ'}(\text{red}, 1, \text{soln})$ and $E^{\circ'}(\text{red}, 2, -\text{soln})$), corresponding to the sequential addition of electrons to each of the bipyridine ligand π^* orbitals (Equations 1,2), are also similar within each group, ranging from -1.30 to -1.36 and from -1.47 V to -1.58 V, respectively.



Irreversible reductions localized at the polymerizable ligands (represented by $E^{\circ'}(\text{red}, 3, \text{soln})$ and $E^{\circ'}(\text{red}, 4, \text{soln})$) can also be observed at more negative potentials. The process corresponding to Equation 3 is well-defined for the vpy (Figure 3g) and py_2C_2 monomers, whereas the fourth reduction can only be seen clearly in the electrochemistry of the py_2C_2 complex (Figure 3h).



The highest energy peak at 375 nm in the spectrum of $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$ is probably the optical transition corresponding to the fourth electrochemical reduction.

Table 3. Reduction Potentials for the Free Ligands^(a).

	$E_{p,c}$	$\frac{i_{p,a}}{i_{p,c}}$
vpv	-2.27	0
BPE	-1.86 ^(b)	0.60
py ₂ C ₂	-1.92 ^(b)	0

(a) 0.1 M TEAP/CH₃CN electrolyte.

(b) A second, quasi-reversible reduction process is observable for these ligands at potentials ca. 250 mV more negative, presumably due to conversion of the radical anion to the dianion (36).

Table 4. Electrochemical Properties of the Complexes^(a,b).

	<u>[Ru(bpy)₂(L)₂]²⁺</u>			<u>[Ru(trpy)(L)₃]²⁺</u>		
	<u>vpv</u>	<u>BPE</u> ^(c)	<u>PY₂C₂</u>	<u>vpv</u>	<u>BPE</u>	<u>PY₂C₂</u>
E ^{o'} (ox,soln) ^(d)	+1.25	+1.29	+1.33	+1.23	+1.26	+1.32
E ^{o'} (ox,surf)	+1.22	+1.24	+1.32	+1.21	+1.24	+1.32
E ^{o'} (red,1,soln)	-1.36	-1.36	-1.30	-1.24	-1.22	-1.22
E ^{o'} (red,2,soln)	-1.54	-1.58	-1.47 ^(e)	-1.72 ^(e)	-1.50 ^(e)	-1.52 ^(e)
E ^{o'} (red,3,soln)	-1.94 ^(e)	-1.71 ^(e)	-1.73 ^(e)	----	----	----
E ^{o'} (red,4,soln)	----	----	-1.85 ^(e)	----	----	----
(Γ/Γ _o) ₁	1.0	0.4-16	72-173	5-12	6-14	34-46
(Φ _{poly}) ₁ ^(f)	0.3	0.2-1.7	11-25	1.4-2.3	0.9-2.0	4-5
(Γ/Γ _o) ₂	3.7	1-4	310-640	200-310	160-460	250-370
(Φ _{poly}) ₂	1.1	0.3-0.5	48-99	58-60	45-65	28-42
(Γ/Γ _o) ₃	320-360	2.3	400-410	----	----	----
(Φ _{poly}) ₃	38-43	3.3	63	----	----	----
(Γ/Γ _o) ₄	----	----	430-600	----	----	----
(Φ _{poly}) ₄	----	----	67-92	----	----	----

(a) 0.1 M TEAP/CH₃CN electrolyte, except as noted.

(b) Parameters are explained in the text.

(c) 0.1 M TBAH/CH₃CN electrolyte.

(d) All potentials are in volts vs. SSCE.

(e) Irreversible reduction, value of E_{p,c}.

(f) All polymerization efficiencies are reported in units of percent.

Solutions of the polymerizable complexes were subjected to oxidative potential cycling. After numerous cycles (typically many tens to hundreds) through the Ru(III/II) couple, subtle hints of irreversibility appear in the CV. Examination of the electrodes used in these experiments in fresh electrolyte reveal the presence of up to a few monolayers of electroactive material at $E^{\circ'}$ values corresponding roughly to the particular monomer used. Efficiencies for oxidative film formation are low, the highest value being several tenths of 1% for the bis(BPE) complex (24). This feature will be discussed further in the section on the tris(L) complexes.

Repeated cycling of the potential applied to the working electrode through the first bipyridine reduction results in the slow, but steadily increasing current at $E^{\circ'}$ (red,1) due to the reduction of both monomer in solution and the metal complex sites in the incipient polymer film (9,11) (Figures 3a,c,e). During EP of the py_2C_2 complex a cathodic prewave (or quasi-reversible couple) develops, initially at -1.0 V, which increases in size and gradually shifts to more negative potentials with continued cycling. The origin of this feature is unknown, but it occurs only with the acetylenic monomers. Similar CV behavior is observed when the potential sweep includes the second bpy reduction (Figures 3b,d,f). The more rapidly increasing current indicates faster film growth, especially for the py_2C_2 complex which again displays an apparent growing, shifting couple at potentials positive of the first bpy reduction wave. If the EP experiment is carried out by cycling through the polymerizable ligand reductions (Figures 3g,h), film growth is much faster than by cycling through either of the bpy couples.

Following EP, the coated electrodes were rinsed in acetone, then transferred to a solution of fresh supporting electrolyte. In Figure 4, Curve A, is a representative example of a steady-state potential scan between 0 and +1.8 V of the surface-bound

metallopolymers which show the Ru(III/II) couples (and associated prewaves) at $E^{\circ'}(\text{surf}) = +1.22 \text{ V (vpy)}, +1.24 \text{ V (BPE)}$ and $+1.32 \text{ V (py}_2\text{C}_2\text{)}$. The observed responses are nearly Nernstian in character for surface-immobilized species, as demonstrated by the 30 mV peak splitting and linear anodic peak current vs. sweep rate behavior, plotted as $\log(i_p)$ vs. $\log(v)$, the slope equals "m" in the expression $i_p \propto v^m$ ($m = 1.03$, see upper inset, Figure 4). Curve B in Figure 4 shows the bpy reduction waves for the metal complex sites in the film as a result of repeated potential cycling from 0 to -1.95 V.

In Figure 4, Curve C, is shown the response obtained from cycling the potential applied to the $\text{poly}[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$ coated electrode between +1.8 and -1.95 V in 0.1 M TEAP/ CH_3CN . In addition to the expected metal oxidation and bpy reduction waves, the CV of this single-component film displays the enlarged, exponentially-rising (linear $\log i$ vs. E , see Figure 4, upper inset) prewaves observed (11c) for a single-component $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}$ (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridine) film. Numerous attempts have been made to account for the origin of the prewaves. An early explanation (11c) proposed the existence of dilute, reductively-altered sites distributed throughout the film, which would give rise to the observed "bilayer-like" charge trapping and untrapping peaks. It has since been found that prewaves are also present in the CV of films prepared by oxidative deposition techniques (see below and references 10n,27). Although chemically altered sites may also be formed during the oxidative film-forming reaction, it is unlikely that they would have a reduction potential sufficiently negative of the Ru(III/II) couple to produce the trapped charge situation.

A second proposal is that the prewaves arise from structural changes in the film. If portions of the film exist as highly unswollen domains in the Ru(II) state, then the CV would reflect

the phase-like behavior of such sites (which is characterized by sharp, exponentially-rising peaks) in a manner similar to that observed in a number of other systems (10g,11h,28), e.g., oxidation of a poly(vinylferrocene) film in aqueous electrolyte. However, the lack of any reverse component associated with deswelling upon return to the Ru(II) state casts doubt upon this hypothesis as well.

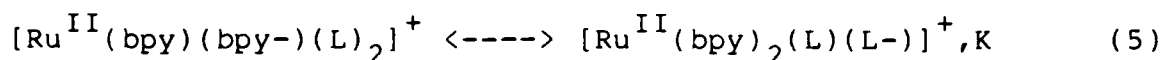
The poly-bis(L) complex films are quite stable with respect to oxidative cycling. The durability of the polymer derived from $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$ has been previously noted (11a,b). For the film formed by EP of the py_2C_2 complex, a decrease in electroactivity of 20% was observed after 186 cycles through the Ru(III/II) wave at 100 mV/s, corresponding to the film having spent approximately 11 minutes in the Ru(III) state.

The polymerizability, $(\Gamma/\Gamma_0)_1$, and film formation efficiency, $(\Phi_{\text{poly}})_1$, of the vpy and BPE (25) complexes obtained by cycling through the first bpy reduction are much lower than the values obtained for the py_2C_2 complex. Film formation for the latter complex occurs up to 175 times faster than for the reference vpy monomer, with efficiencies of up to 25% (i.e. the charge under the surface wave corresponds to one-fourth of the charge passed during the polymerization reaction).

EP at the second bipyridine reduction has only a modest effect on the rate of film formation. Although the $(\Gamma/\Gamma_0)_2$ values for the py_2C_2 complex are numerically much larger than $(\Gamma/\Gamma_0)_1$, 310-640 vs. 72-173, the approximate factor of four increase is almost identical to that observed for the vpy complex, where the polymerizability improved by a factor of 3.7. However, the high polymerizability of the bis(pyridyl)acetylene complex, at both the first and second reductions, is still unusual for a bis(polymerizable ligand) monomer as comparison to the vpy and BPE complexes

demonstrates. The value of 640 for $(\Gamma/\Gamma_0)_2$ is an order of magnitude larger than that for any other disubstituted monomer complex previously reported (9).

For the bis(L) complexes, EP effected at the bpy reductions is thought to occur via "indirect initiation" - an activated process wherein an electron located in a π^* (bpy) orbital is in intramolecular redox equilibrium with the π^* orbital of the polymerizable ligand located ΔE higher in energy (Equations 5,6). Therefore, the polymerizability is related to the difference



$$K = 10^{(-16.9 \Delta E)} \quad (6)$$

in energy of the bpy and L reduction potentials. With the detection of the polymerizable ligand reduction potentials in CV, ΔE can be obtained both from spectral and electrochemical experiments, as shown in Table 5. Correlations between the ΔE values for a particular complex are in good qualitative agreement (26), although the energy differences measured optically are generally greater than electrochemical values. This discrepancy is because the optical transition is to the higher energy singlet charge transfer state, whereas electrochemical reduction produces the lower, thermally-equilibrated triplet state.

From ΔE considerations alone, both the BPE and py_2C_2 monomers should show much greater (Γ/Γ_0) values than $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$, yet in fact only the acetylenic complex does. For example, the ratio of K (which reflects the concentration of the polymerizable ligand radical anion and hence the rate of polymer formation) for the BPE complex relative to the vpy complex, using the electrochemical ΔE values, is approximately 10^4 . The low polymerizability of the bis(BPE) complex indicates that (Γ/Γ_0) is a composite

Table 5. Comparison of the Optical and Electrochemical Reduction Potentials of the Bound Ligands in the $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ and $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ Complexes.

	<u>Optical</u> ^(a)			<u>Electrochemical</u> ^(b)		
	<u>bpy(0/-)</u>	<u>L(0/-)</u>	<u>DELTA E</u>	<u>bpy(0/-)</u>	<u>L(0/-)</u>	<u>DELTA E</u>
vpy	2.67, 2.86	3.46	0.79, 0.60	-1.36, -1.54	-1.94	0.58, 0.40
BPE	2.69, 2.90	3.14	0.45, 0.24	-1.36, -1.58	-1.71	0.35, 0.13
py ₂ C ₂	2.73, 2.92	3.16	0.42, 0.24	-1.30, -1.47	-1.73	0.43, 0.26
	<u>trpy(0/-)</u>	<u>L(0/-)</u>	<u>DELTA E</u>	<u>trpy(0/-)</u>	<u>L(0/-)</u>	<u>DELTA E</u>
vpy	2.48	3.34	0.86	-1.24	-1.72	0.48
BPE	2.48	3.07	0.59	-1.22	-1.50	0.28
py ₂ C ₂	2.50	3.12	0.62	-1.22	-1.52	0.30

(a) Transition energies are in volts.

(b) Reduction potentials are in volts vs. SSCE.

parameter, of which ΔE is an important, although not necessarily determining factor. Two considerations may contribute to this observation. First, $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^{2+}$ is significantly less soluble in perchlorate electrolyte than either of the other complexes. If EP of the $\text{bis}(\text{py}_2\text{C}_2)$ complex forms a conjugated polymeric structure, the individual units of the polymer would resemble the BPE monomer and therefore reflect its lower solubility. A second factor to consider is the reversibility of polymerizable ligand reduction. Table 3 gives the ratio of the anodic to cathodic peak currents, $(i_{p,a}/i_{p,c})$, for the free ligand $\text{L}(0/-)$ couples in acetonitrile solution. These values show that no reverse component is observed after reduction of vpy and py_2C_2 at sweep rates of 200 mV/s. However, the BPE ligand reduction is partially reversible, indicating a somewhat more stable radical anion. This feature may be carried over in the Ru-bound ligand and would have a direct bearing on the lower polymerizability of the complex.

A particularly interesting feature of the py_2C_2 complex is the polymerization efficiency at the second reduction. $(\phi_{\text{poly}})_2$, which has been found to be as high as 99% in several EP reactions, has been employed to support arguments concerning the mechanism of reductive EP (9). Previously reported values of ϕ_{poly} for $\text{bis}(\text{L})$ complexes ranged as high as 8 to 12% - already much higher than would be expected based on ΔE and K alone. Steps were included in the EP mechanism which involved recycling the electron initially used to reduce the monomer complex in various chain processes. The observed value of ϕ_{poly} , which is directly proportional to Γ , is necessarily a lower limit because Γ accounts only for the polymeric material which ultimately accretes onto the electrode and does not account for any soluble, oligomeric products. It could reasonably be expected that some polymerization reactions are more than 100% efficient and efficiency values greater than 100% REQUIRE invocation of a chain growth process as at least part

of the overall EP mechanism. However, for all the polymerizable monomers investigated to date, the maximum efficiencies do not exceed 100%, within experimental error. Therefore, while chain pathways must contribute to some extent, sequential hydrodimerization of the reactive polymerizable ligand radical anions is most likely the dominant (and limiting) route to metallopolymer formation.

The observation of the polymerizable ligand-based reductions in the bis(L) monomers also supports the mechanism described above. Complexes which are found to be difficult to polymerize at the bpy reductions become good monomers under conditions of direct initiation. However, although Φ_{poly} values are much higher, they still never exceed unity. Another ramification of the direct initiation results is that $(\Gamma/\Gamma_0)_3$ appears to be relatively insensitive to the nature of the polymerizable ligand. While this is beneficial in terms of providing an effective means of producing good coatings of any bis(L) monomer, it also greatly reduces the potential for increasing complex polymerizabilities by virtue of improved synthetic design.

The rate of charge transport through the poly-[Ru(bpy)₂(py₂C₂)₂]²⁺ film was measured as the diffusion coefficient, D_{ct} , by chronoamperometry. The applied potential step was sufficient to cause oxidation of the sites in the film from Ru(II) to Ru(III). Initial potentials ranged from +0.6 to +1.0 V, final potentials were +1.6 to +1.9 V. A typical chronoamperogram and resulting Cottrell plot are shown in Figure 5. D_{ct} was found to be independent of the final potential beyond approximately +1.6 V. The anodic current for the Ru(II) → Ru(III) reaction was plotted vs. $t^{-1/2}$, and D_{ct} was calculated from the linear short-time slope using the Cottrell equation. The concentration of the Ru sites, $C(\text{Ru})$ was estimated to be 1.3×10^{-3} mol/cm³ from the molecular weight of the monomeric Ru complex unit (977 g/mol) and using 1.3

g/cm³ for the density of the metallopolymer, by analogy to the value of 1.35 g/cm³ measured for the density of samples of poly-[Ru(vbpy)₃]²⁺ (11b). D_{ct} ranged between $2.4 - 4.0 \times 10^{-9}$ cm²/s, in agreement with values for numerous other electrochemically polymerized films of vinyl monomers (11b,g). It is distinctly different, though, from D_{ct} measured for the oxidation of neutral poly(acetylene) which is slower by approximately three to four orders of magnitude (29).

(c) Microscopy

The morphology of the metallopolymer films was investigated by scanning electron microscopy. Figure 6 shows SEMs of poly-[Ru(bpy)₂(py₂C₂)₂]²⁺ coated onto a Pt foil electrode. The internal structure of the film appears dense and homogeneous, as shown by the cross-section views. The dimensions of surface features, which take the form of amorphous balls and ridges of polymer, are small compared to the thickness of the film. Pores or pinholes in the top surface of the film are not observable at this magnification (4000x), although cracks are present at the outer edges. There is no evidence for a fibrillar structure typical of poly(acetylene) films (30), a feature which would be observable at this magnification.

(d) Conductivity Studies

Two-point conductivity measurements were performed on the dry film-coated electrodes as described in the Experimental Section. Film resistances, R_f , were found using both methods to be in the range $10^9 - 10^{10} \Omega$. For an electrode area of 1.8×10^{-2} cm² and a film thickness, d , of ~ 1 micron, the conductivity of the film, σ , can be calculated from the relationship, $\sigma = d/AR_f$ to be approximately $10^{-12} \Omega^{-1} \text{cm}^{-1}$. This value compares favorably with σ of ca. $10^{-11} \Omega^{-1} \text{cm}^{-1}$ for a poly-[Ru(vbpy)₃]²⁺ film, which was estimated from the reported film resistance (31). The poor conductivity of the polymer films formed from the bis(pyridyl)acetylene

complex is somewhat disappointing given the presumably conjugated backbone of the metallopolymer chain or network. The reason for this may have two origins. First, reduction of the acetylenic complex to form a conjugated polymer may have been followed by further reduction of the remaining olefinic sites to produce a saturated system. Attempts to obtain structural information about the polymer are underway. Second, a number of $(CH)_x$ derivatives such as poly(phenylacetylene) have been prepared and the doped versions of the substituted materials are found to be less conductive than the analogously doped parent polymer (32). In the present case, substitution of the conjugated chain (if one is actually present) in addition to the fact that the metallopolymer almost certainly has a network, rather than linear structure, may be the cause of the low conductivity.

By comparison, neutral poly(acetylene) is not a much better conductor. σ for trans- $(CH)_x$ is $10^{-5} \Omega^{-1}cm^{-1}$; cis- $(CH)_x$ is $10^{-9} \Omega^{-1}cm^{-1}$ (14). Conductive $(CH)_x$ is only obtained upon partial oxidation or reduction of the $(CH)_x$ π -network. Similarly, many linear chain conductors or other quasi one-dimensional materials such as the partially-oxidized tetracyano platينات, TTF/TCNQ and various phthalocyanine polymers owe their conductivity to their partially oxidized, or mixed valence, characters (33). With this fact in mind, the conductivity of the reduced mixed valence poly- $[Ru(bpy)_2(py_2C_2)_2]^{2+}$ film was investigated.

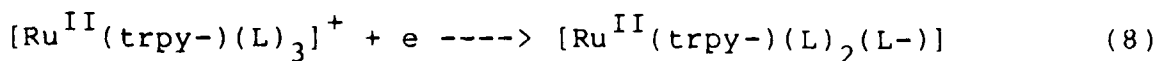
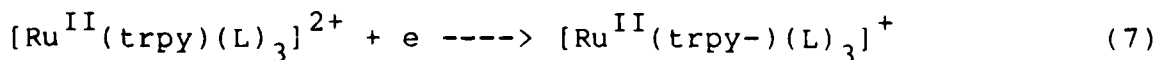
The mixed valence polymer was prepared by fixing the electrode potential at -1.23 V, which is $E^{O'}$ (red,1) for the surface-bound complex (see Figure 1). Visual inspection of the partially reduced film showed a distinct darkening from the initial gold color. The conductivity of the mixed valence film was determined as described in the Experimental Section. The films were then oxidized to the 2+ form (restoring the gold color) and the conductivity re-measured. The results from the conductivity experiments were of two types. In most cases, σ for the

mixed valence and subsequently oxidized films remained in the neighborhood of $10^{-12} \Omega^{-1} \text{cm}^{-1}$. Several of the mixed valence films showed large decreases in film resistance, with R_f being less than 1Ω . However, after re-oxidation R_f remained less than 1Ω , not returning to the $10^9 - 10^{10} \Omega$ range expected for the film in the 2+ stage. It was therefore concluded that the mixed valence state is NOT electrically conductive and that the observed decrease in R_f for some films was probably caused by minor chemical or physical degradation or restructuring of the film in the mixed valence form which leads to shorting of the Pt electrode and Hg contact.

(e) The Trisubstituted Complexes, $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$: Spectral and Redox Properties

The UV-Vis spectra of the tris(L) homologs are shown in Figure 7; peak maxima are listed in Table 2. By analogy to other Ru(II)-terpyridine complexes (27,34) and to the closely related Ru-bpy systems, the lowest energy bands at ca. 500 nm are assigned as $\pi^*(\text{trpy}) \leftarrow \text{Ru}(d\pi)$ in origin. The well-resolved bands at higher energies (between 372 and 405 nm) are the metal-to-polymerizable ligand charge transfers. As above for the bis(L) complexes, the ordering of the Ru \rightarrow L transition energies remains: $\text{vpy} \gg \text{py}_2\text{C}_2 > \text{BPE}$.

Reduction potentials were obtained from CV experiments. The Ru(III/II) potentials lie between +1.23 and +1.32 V. The first reductions, localized at the trpy ligand (Equation 7), are essentially constant at -1.22 to -1.24 V. The irreversible reductions of the polymerizable ligands (Equation 8) are easily



observable, ranging from -1.52 to -1.72 V in the sequence listed above, and correlate well with optical measurements. The cathodic peak potentials, $E_{p,c}$, for the individual complexes occur ca. 200 mV more positive than for the analogous bipyridine monomers, reflecting the absence of a second polypyridine ligand reduction prior to the $L(0/-)$ process.

EP of the complexes was carried out by either constraining the negative potential limit to encompass only the $trpy(0/-)$ couple or by including the $L(0 \rightarrow -)$ process in the sweep as well. These correspond, respectively, to the indirect and direct initiation cases discussed in the section on $bis(L)$ complexes. CVs of the film-formation reaction are shown in Figure 8. When potential cycling is confined to the $trpy$ reduction only (Figures 9a,c,e), the CV displays the normal slow, steadily increasing growth observed for complexes such as $[Ru(bpy)_2(vpy)_2]^{2+}$ and $[Ru(vbpy)_3]^{2+}$. Values for $(\Gamma/\Gamma_o)_1$ are moderate, ranging from 5 to 50, the acetylenic monomer again being the easiest to polymerize. Extending the negative sweep limit beyond the polymerizable ligand reduction (Figures 8b,d,f) gives rise to the rapidly growing, shifting wave pattern seen, for example, during EP of the $bis-(py_2C_2)$ complex. As was the case for the $bis(L)$ complexes, polymerizability at the ligand-based reductions is high $((\Gamma/\Gamma_o)_2 = 160-460)$, but relatively insensitive to which polymerizable ligand is involved. This is an indication that steric hindrance from coupling of pyridyl-substituted monomers plays a less important role than other factors in the overall polymerizability of a complex. The continual shifting of the waves to more negative potentials during the direct initiation experiments can most likely be accounted for by IR losses, due to slower charge transport through the fast-growing, increasingly thicker and more highly cross-linked incipient film (35).

CVs of the films derived from direct initiation of the trpy monomers exhibit the unusual feature of two apparently overlapping peaks in the potential region corresponding to the Ru(III/II) couple. This effect is most pronounced for the tris(BPE) complex, shown in Figure 9. The major component of the two occurs at ca. +1.24 V, the minor component at about +1.29 V. Only the former couple is observed in films formed by EP at the trpy reduction. The similarity of E^0 for the minor component to that for the solution monomer suggests that the more positive potential couple may arise from incompletely polymerized Ru complex sites which are incorporated into the polymer network under conditions of rapid film growth. The presence of multiple couples in a film produced by EP of a single monomer also raises questions about interpretation of the behavior of other similar, ostensibly single-component films in electrocatalysis or charge trapping applications.

The $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ complexes were also subjected to oxidative potential cycling. The oxidative electrochemical characteristics of the tris(L) monomers and polymers are summarized in Table 6. As shown in Figure 10a for the BPE complex, repeated sweeps between 0 and +1.7 V result in rapid growth and distortion of the Ru(III/II) couple, reminiscent of the reductively-initiated film formation reaction described above. The CV of the resulting coated electrode in fresh electrolyte (Figure 10b) is rather remarkable in that it is composed of at least three resolvable couples, two of which do not correspond to the potentials observed for either the monomer in solution or the reductively-polymerized films of the same complex.

The film-forming ability of the tris(L) complexes is actually quite respectable, although not as high as when reductive initiation is employed. The anodic oxidation of various organics such as amines (36a,b), phenols(36c), crown ethers (10y), and pyrrole (13), or functionalized transition metal complexes (10n) such as

Table 6. Oxidative Film Formation Characteristics of the $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ Complexes^(a).

	<u>vpy</u>	<u>BPE</u>	<u>PY₂C₂</u>
$E^{o'}$ (soln)	+1.23	+1.26	+1.32
$E^{o'}$ (surf)	+1.24	+1.48, +1.38, +1.30	+1.48, +1.38
(Γ/Γ_o)	1.1	100-130	5-16
Φ_{poly}	0.2	15-18	0.6-1.8

(a) 0.1 M TEAP/ CH_3CN electrolyte.

$[\text{Ru}(\text{5-NH}_2\text{-phen})_3]^{2+}$ (5-NH₂-phen = 5-amino-1, 10-phenanthroline) to yield polymers via established coupling paths is well known. However, films from oxidation of olefinic and acetylenic monomers was unexpected. While it is possible that precipitation of the complex as Ru(III) and slow dissolution of the Ru(II) form may account for the behavior of these complexes, the stability of the coated electrodes in fresh electrolyte solution argues against this explanation. An alternative hypothesis is that an initial metal-centered oxidation could promote an intramolecular ligand oxidation, introducing hydroxyl groups (from trace water in the solvent) which could then couple to form polymers. The resulting oxidized carbon sites in the ligand would also explain the shift to more positive potentials of the metal complex sites in the film. A direct ligand oxidation pathway to give rise to a cationic chain polymerization pathway is not plausible because: (1) the observed $E^{\circ'}$ for the monomer is at the correct potential for the Ru(III/II) couple and (2) no oxidative process is observed for the free ligands up to +2.0 V.

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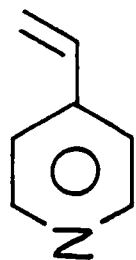
25. Reductive electropolymerization was performed in 0.1 M TBAH/ CH_3CN (see Experimental Section). To determine the affect of PF_6^- on film formation, the bis(vpy) complex was also polymerized in this electrolyte. (Γ/Γ_0) was found to be 1.0 (to within 10%) - the same as in ClO_4^- solution.
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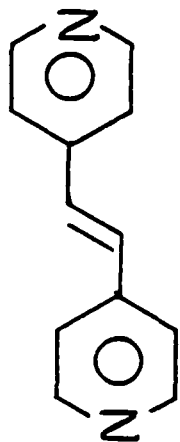
FIGURE CAPTIONS

1. Ligands and complexes used in the electropolymerization experiments.
2. UV-Vis spectra of the $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ complexes in CH_3CN solution, $\text{L} =$ (a) vpy, (b) BPE, (c) py_2C_2 . The concentration of complex used was ca. 10^{-4} M.
3. Reductive Cyclic Voltammetry of the $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$ complexes. Repeated cycling at the first bpy reduction: $\text{L} =$ (a) vpy, (c) BPE, (e) py_2C_2 . Repeated cycling at the second bpy reduction: $\text{L} =$ (b) vpy, (d) BPE, (f) py_2C_2 . Repeated cycling through the polymerizable ligand reductions: $\text{L} =$ (g) vpy, (h) py_2C_2 .
4. Steady-state CVs of a poly- $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$ film-coated electrode. Potential limits used were: curve (A) $0 \leftrightarrow +1.80$ V; curve (B) $0 \leftrightarrow -1.95$ V; curve (C) $+1.8 \leftrightarrow -1.95$ V. Current sensitivity, S , was adjusted for clarity: curve (A) $5 \mu\text{A}$; curve (B) $25 \mu\text{A}$; curve (C) $10 \mu\text{A}$.
5. $I-t$ response of poly- $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$ film to a $+0.6 \rightarrow +1.7$ V. Potential step and resulting Cottrell plot.
6. SEMs of a poly- $[\text{Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2]^{2+}$ film on Pt. (a,b) top view, (c,d) edge view.

7. UV-Vis spectra of the $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ complexes in CH_3CN solution, $\text{L} = (\text{a}) \text{vpy}, (\text{b}) \text{BPE}, (\text{c}) \text{py}_2\text{C}_2$. The concentration of complex used was ca. 10^{-4} M .
8. Reductive Cyclic Voltammetry of the $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ complexes. Repeated cycling through the trpy reduction: $\text{L} = (\text{a}) \text{vpy}, (\text{c}) \text{BPE}, (\text{e}) \text{py}_2\text{C}_2$. Repeated cycling through the polymerizable ligand reductions: $\text{L} = (\text{b}) \text{vpy}, (\text{d}) \text{BPE}, (\text{f}) \text{py}_2\text{C}_2$.
9. Cyclic Voltammetry of a poly- $[\text{Ru}(\text{trpy})(\text{BPE})_3]^{2+}$ coated electrode produced by: indirect initiation (dashed line, $S = 2.5 \mu\text{A}$) and direct initiation (solid line, $S = 1.0 \mu\text{A}$). The three proposed components of the surface wave were resolved by eye.
10. (a) Oxidative EP of $[\text{Ru}(\text{trpy})(\text{BPE})_3]^{2+}$, $S = 2.5 \mu\text{A}$; (b) CV of the resultant electrode, $S = 1.0 \mu\text{A}$.



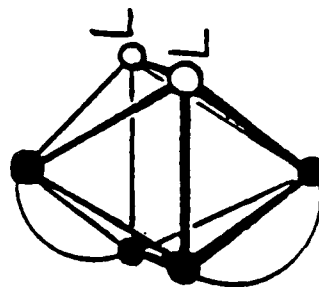
vpy



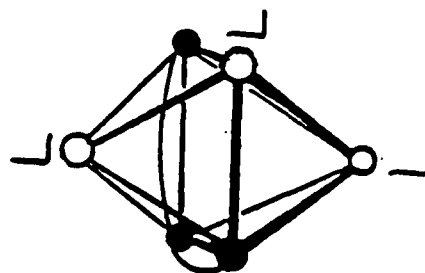
BPE



py₂C₂



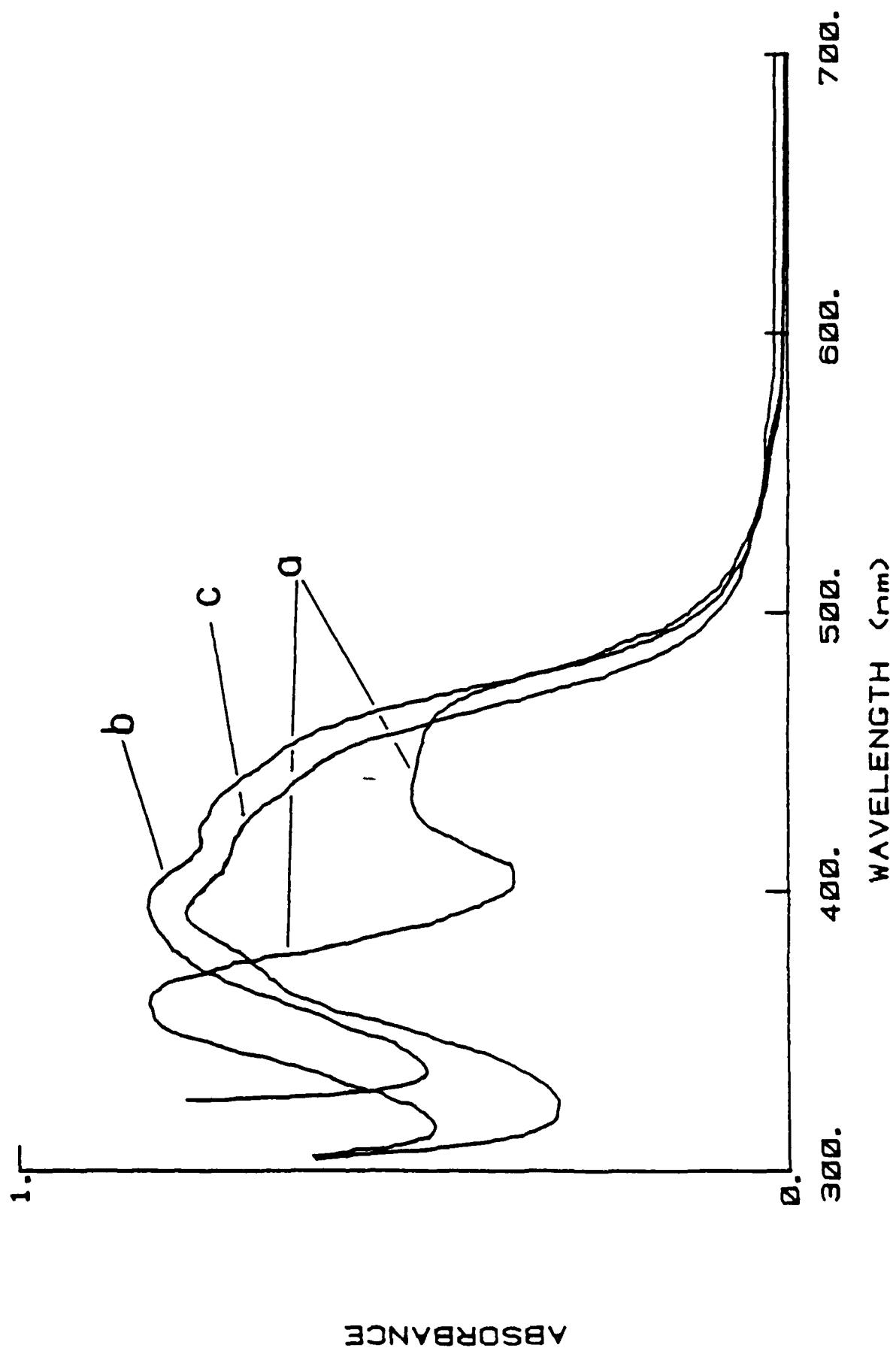
cis - [Ru(bpy)₂(L)₂]²⁺



mer - [Ru(trpy)(L)₃]²⁺

Figure 1.

UV-VIS OF $[Ru(bpy)_2(L)2]^{2+}$ IN CH_3CN



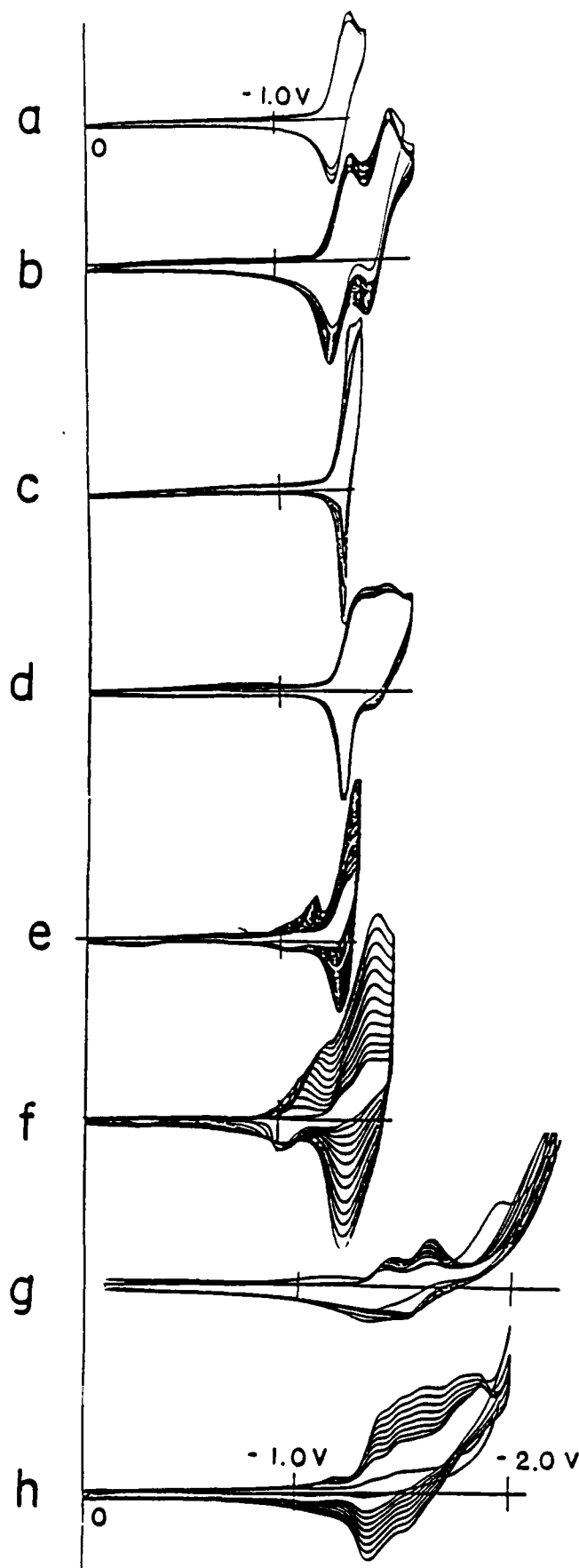


Figure 3.

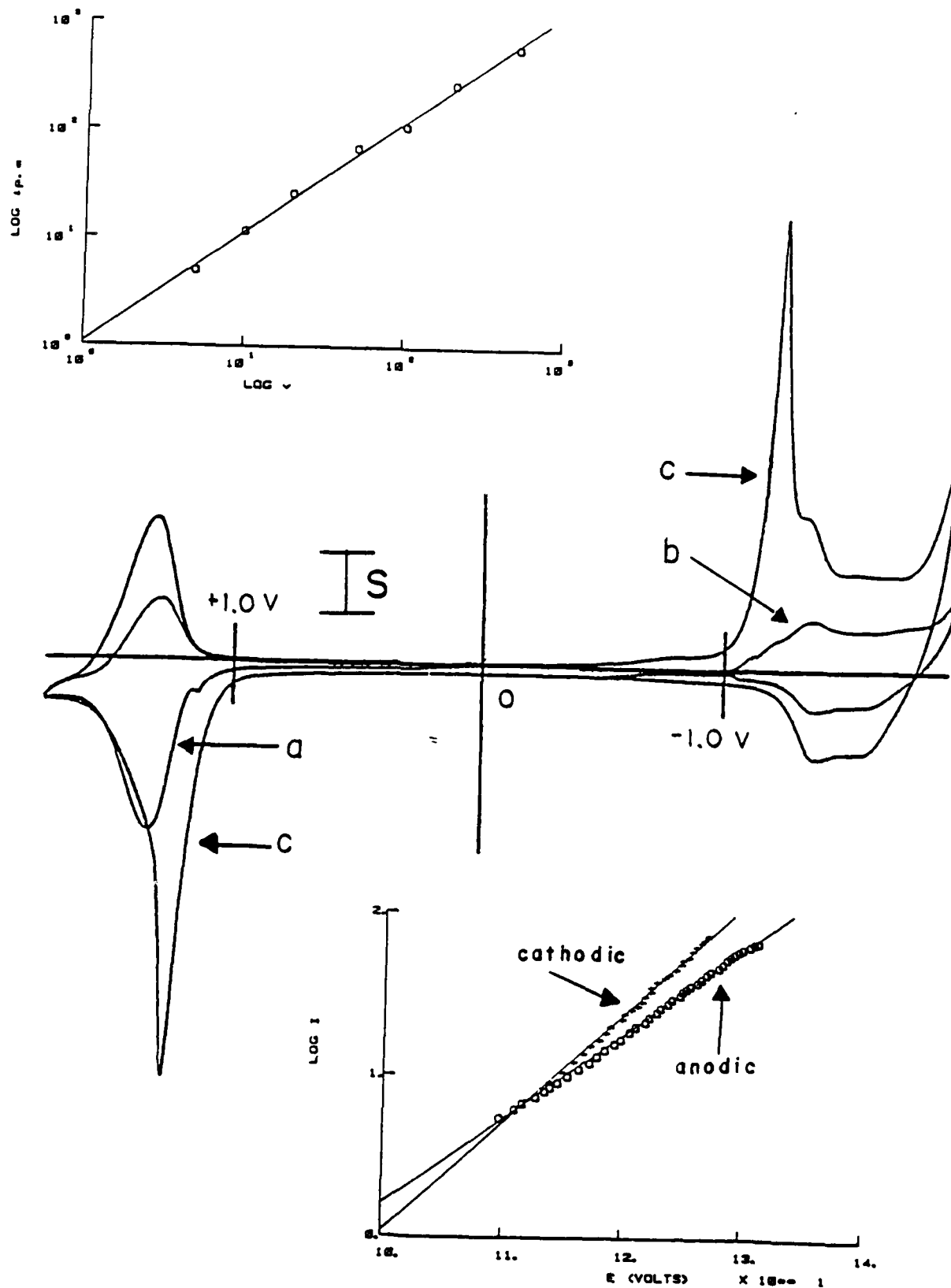


Figure 4.
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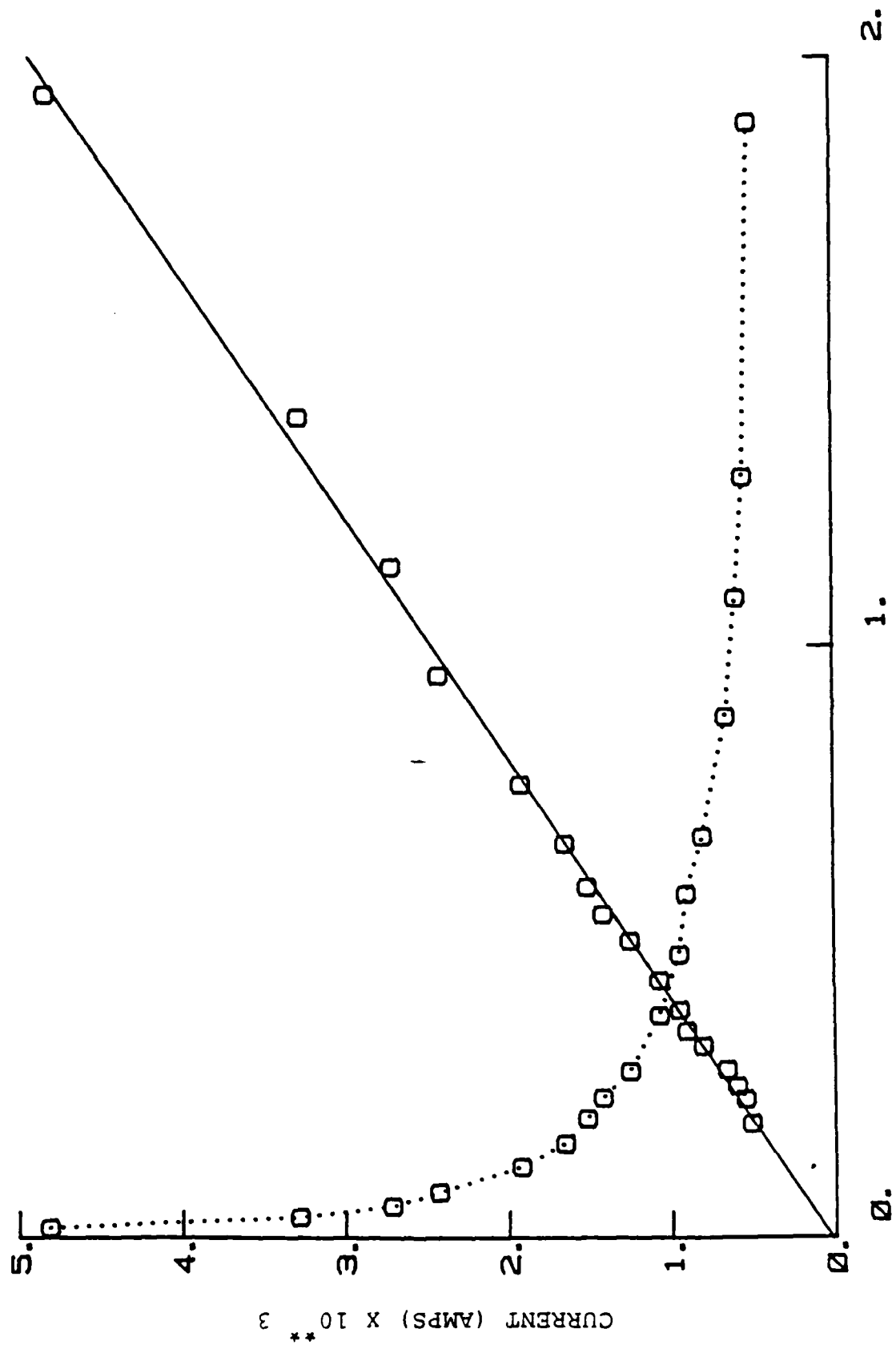


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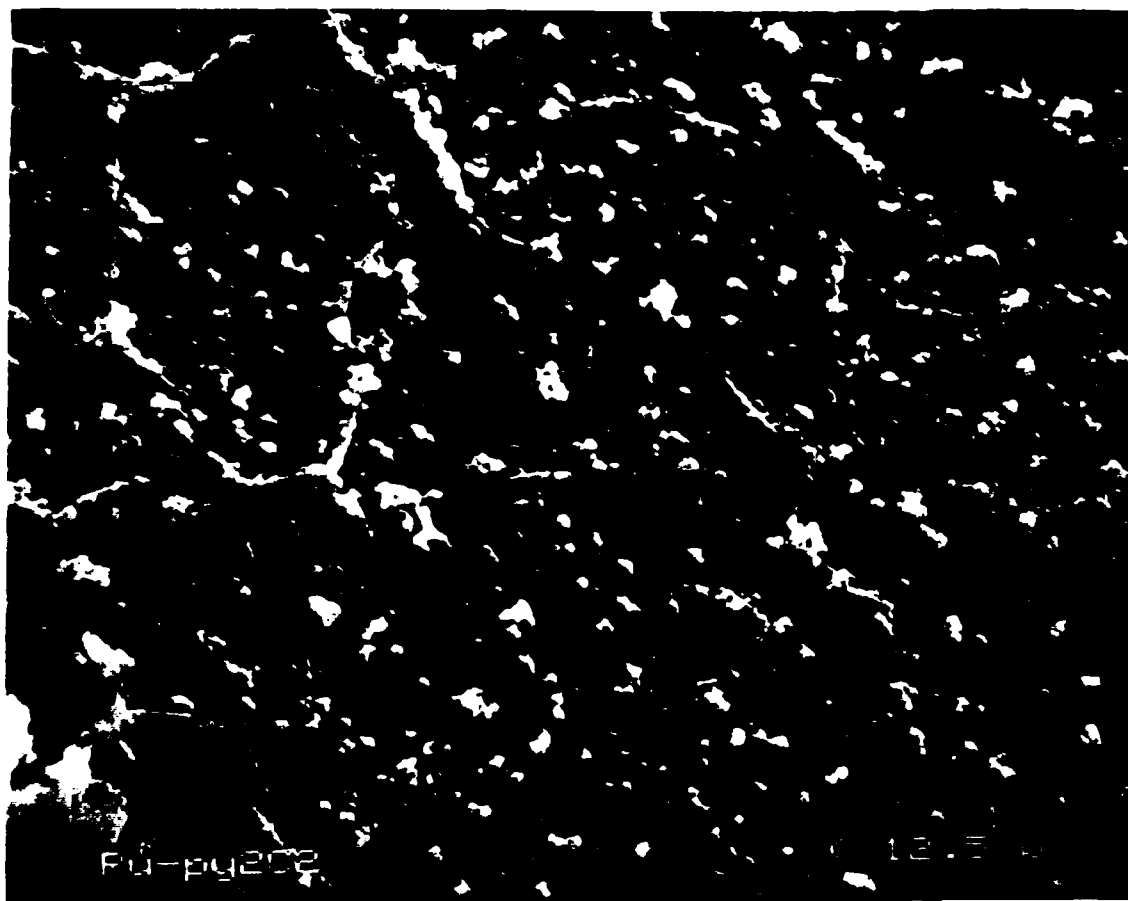


Figure 6(a).

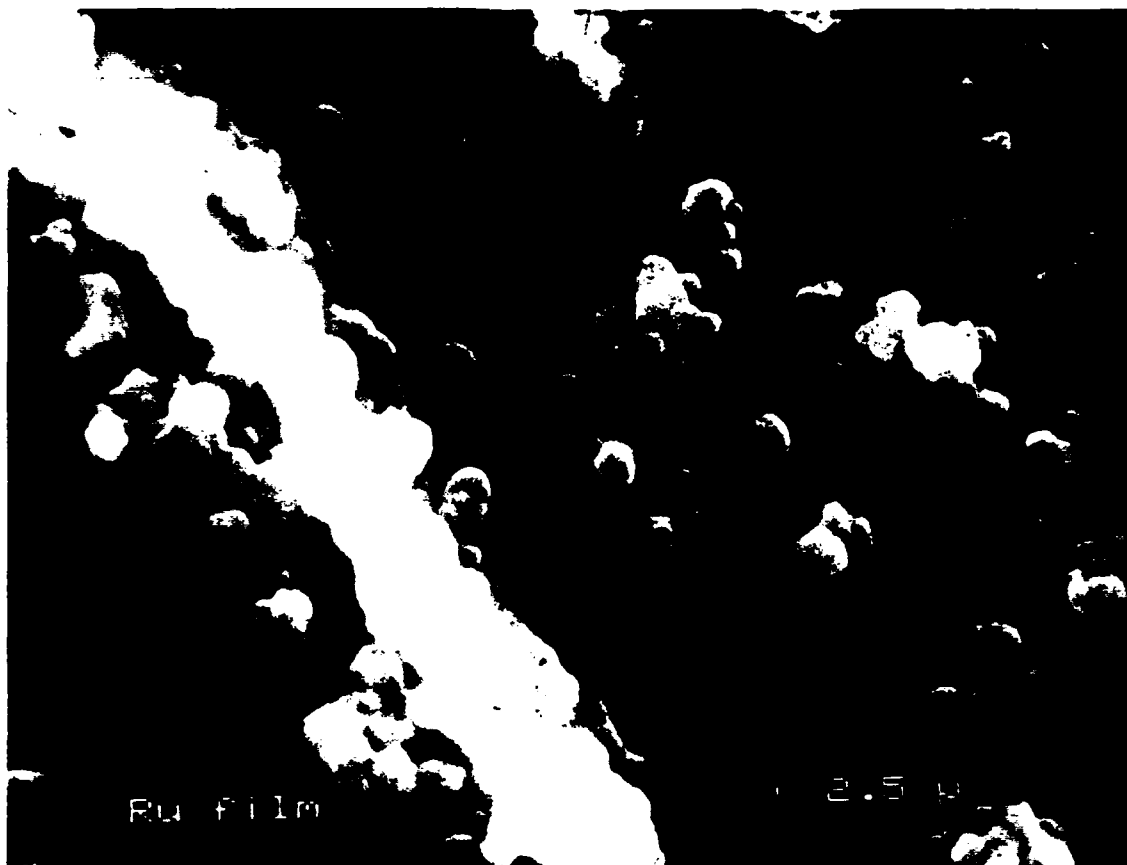


Figure 6(b).

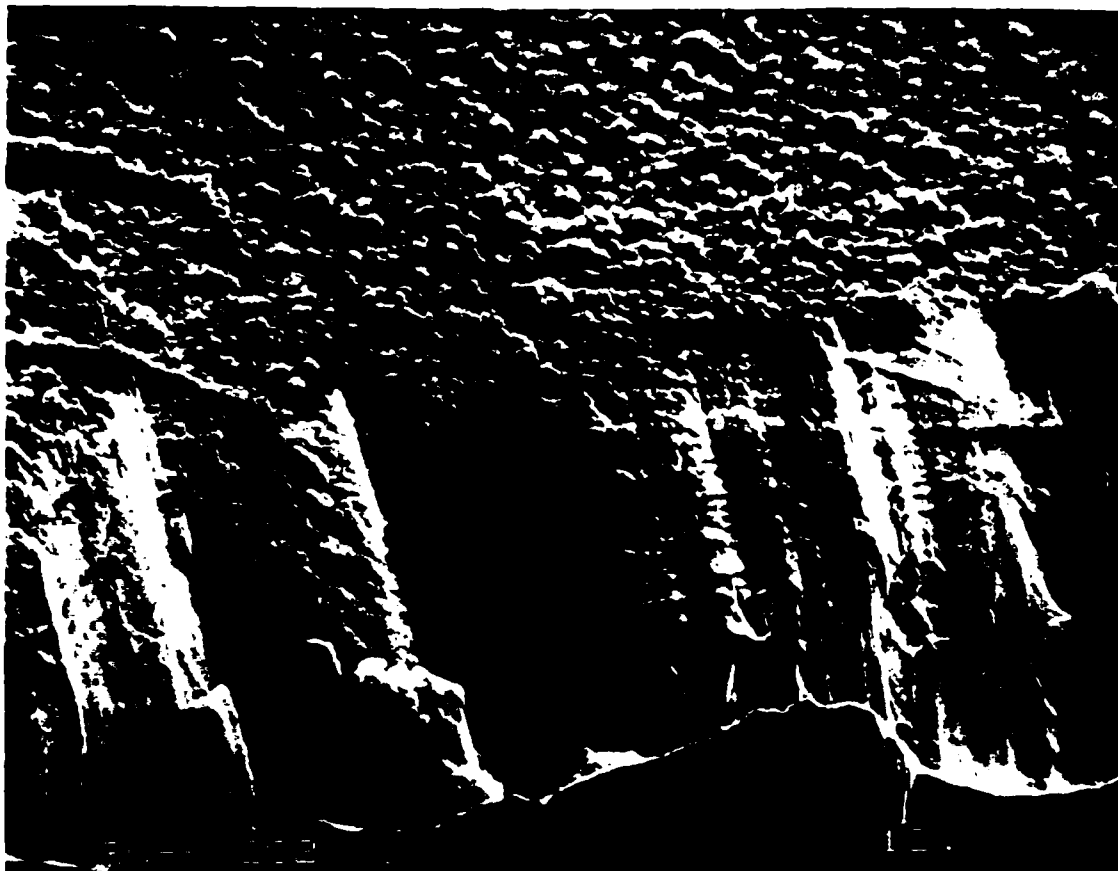


Figure 6(c).

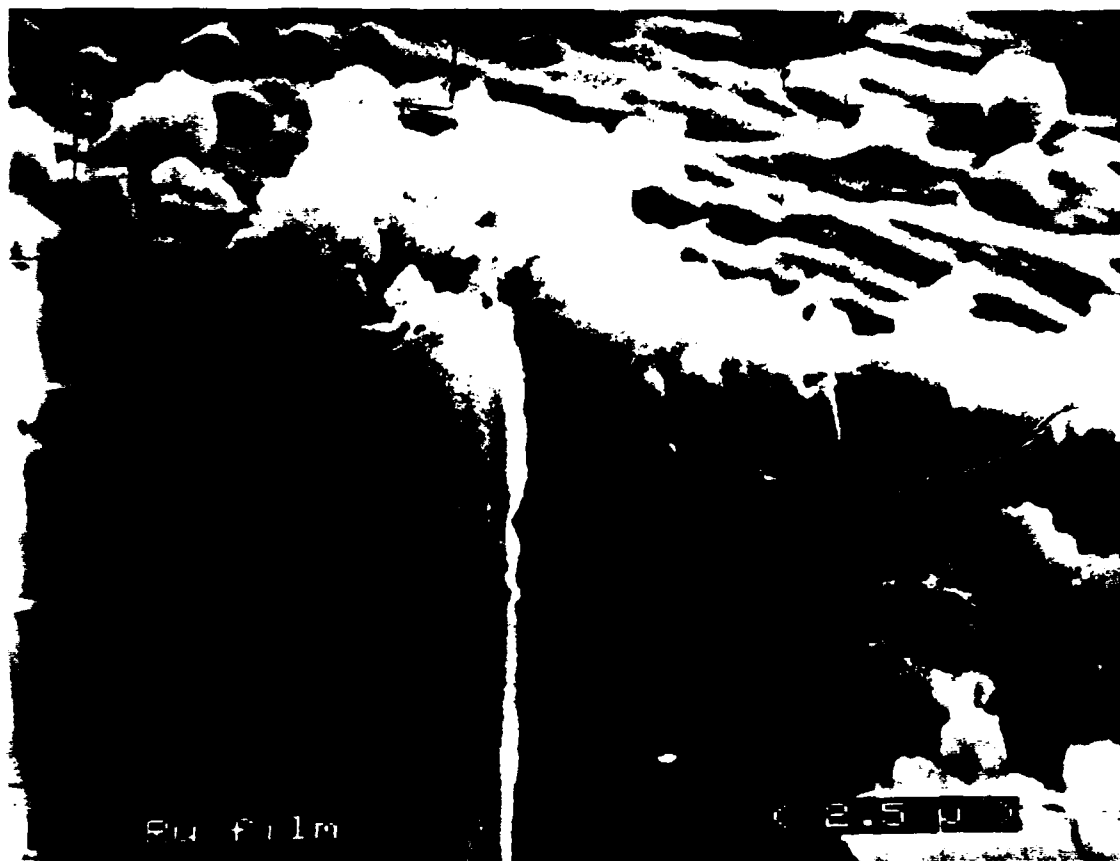


Figure 6(d).

[Ru(trpy)(L)]²⁺ in CH₃CN

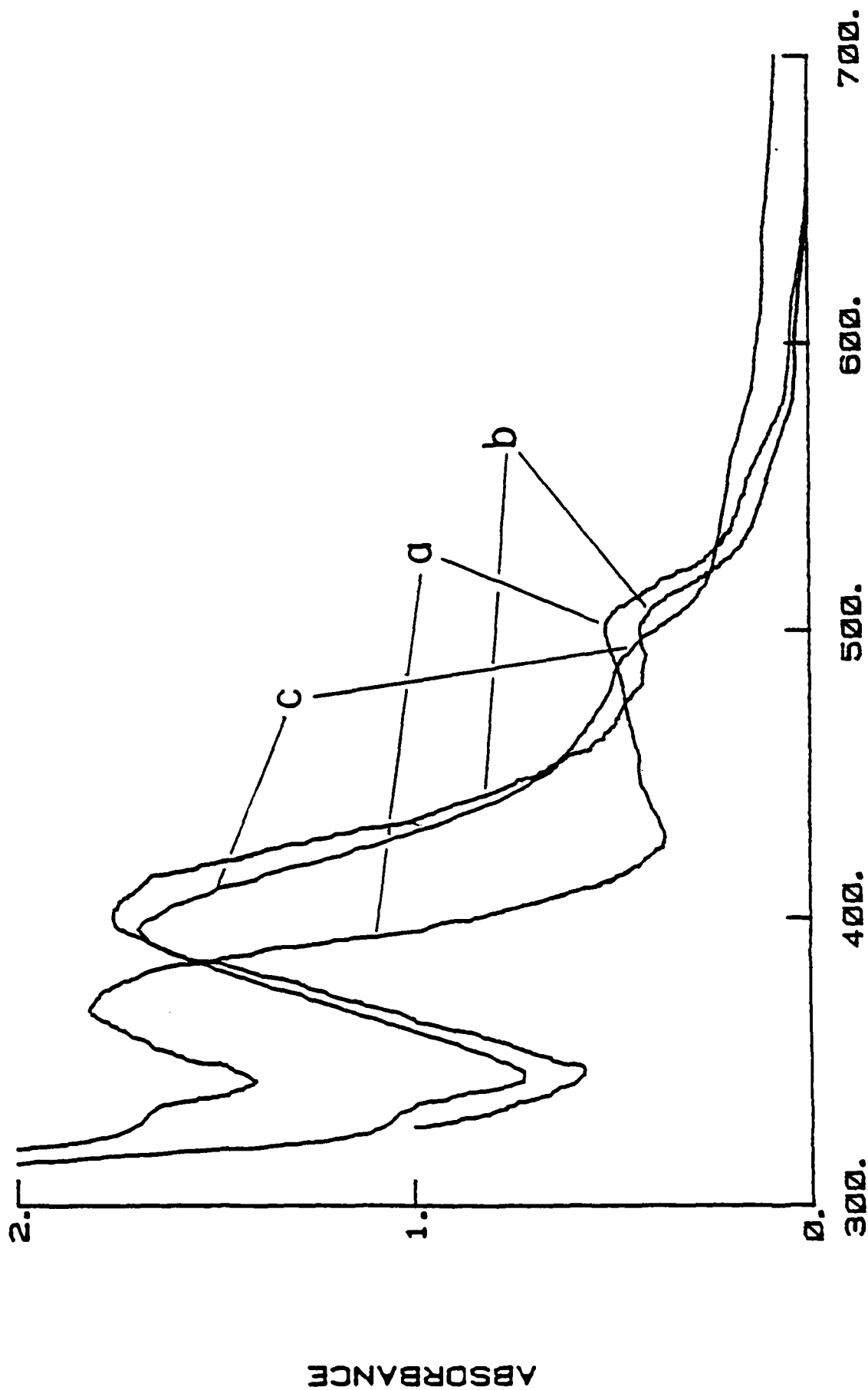


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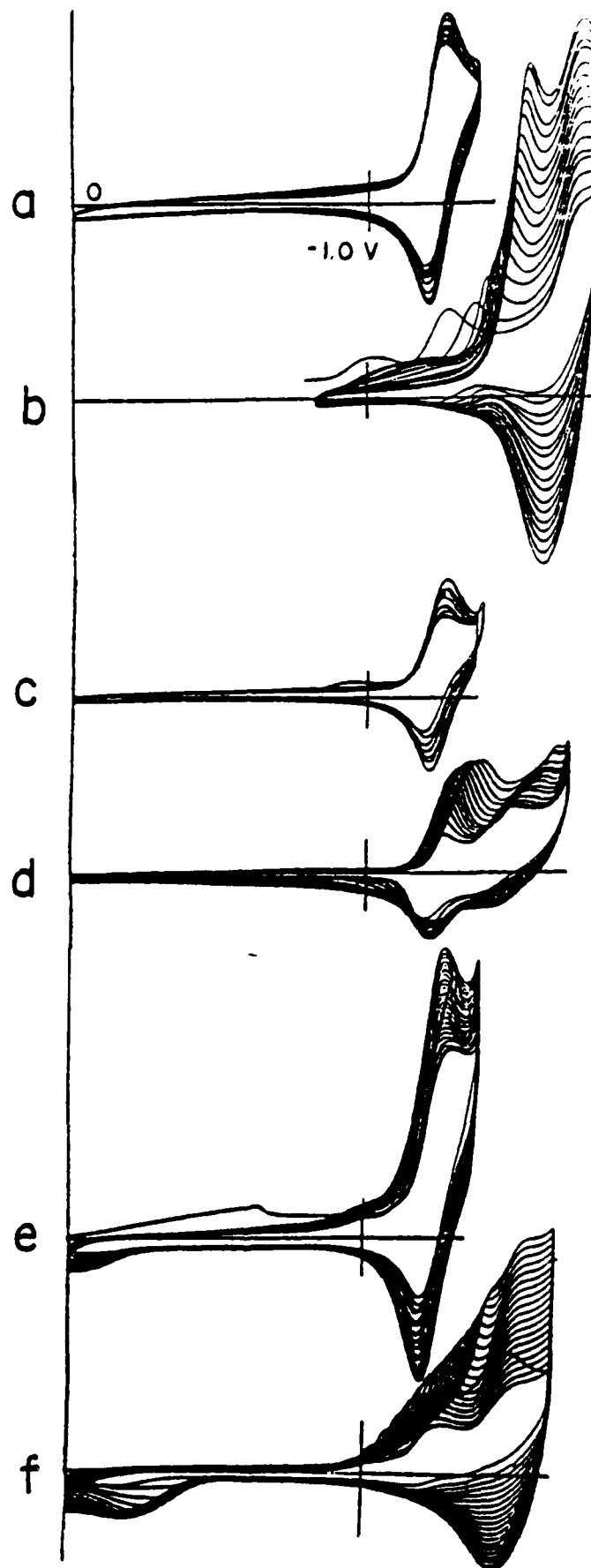


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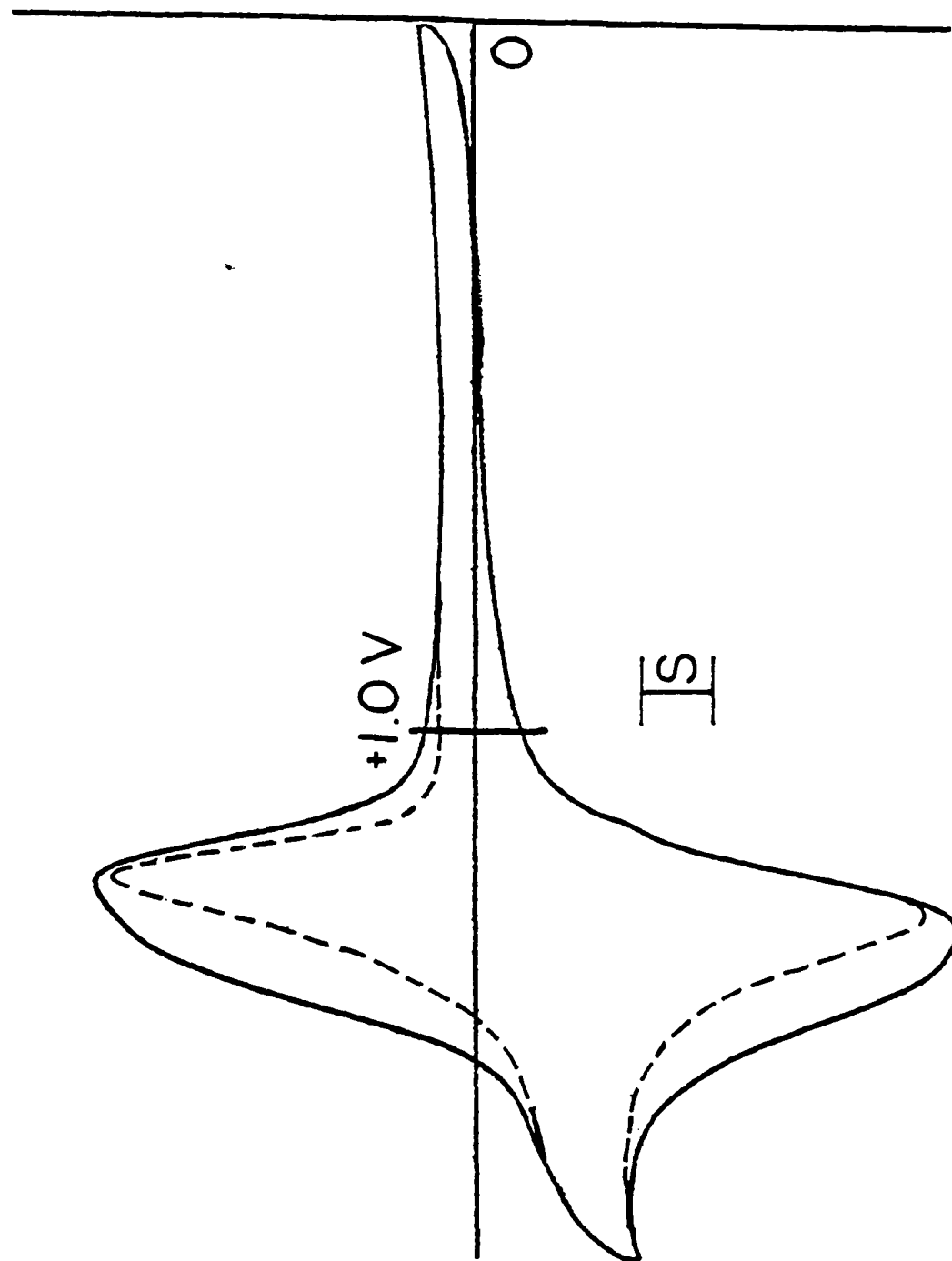


Figure 9.

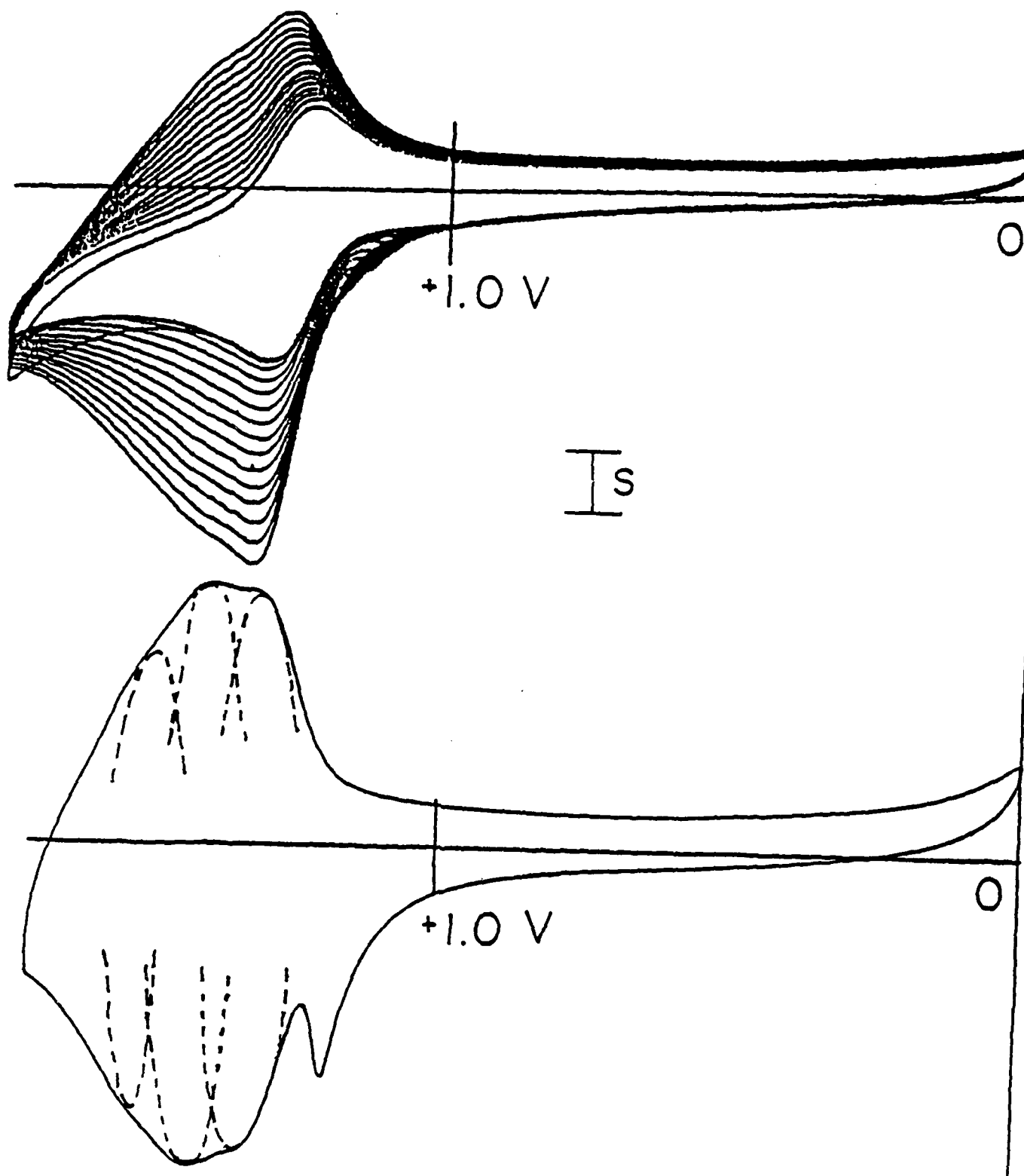


Figure 10.

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